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**EVALUATION OF THE WATER QUALITY SIGNIFICANCE  
OF THE CHEMICAL CONSTITUENTS IN AQUATIC SEDIMENTS:  
COUPLING SEDIMENT QUALITY EVALUATION RESULTS  
TO SIGNIFICANT WATER QUALITY IMPACTS**

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**ABSTRACT**

The US EPA and other regulatory agencies are attempting to develop sediment quality criteria (SQC) that can be used to determine where excessive concentrations of chemical constituents such as heavy metals, chlorinated hydrocarbon pesticides, PCB's, PAH's and other organics are present in sediments at sufficient concentrations and in chemical forms to be significantly adverse to the designated beneficial uses of the waterbody in which the sediments are located. These sediment quality criteria would also be used to modify NPDES discharge limits to restrict the input of those constituents in wastewater discharges and stormwater runoff that accumulate in sediments in excess of the SQC values.

Two of the areas of greatest concern in sediment quality evaluation and management are aquatic life toxicity and the sediments serving as a source of bioaccumulatable chemicals that impair the use of aquatic organisms as food for man and wildlife. At this time, both chemically based and biological impact based sediment quality evaluation procedures are being used to "assess" potentially significant concentrations of toxic and/or bioaccumulatable chemicals in a sediment. These procedures are generating data that indicate that some aquatic sediments contain sufficient concentrations of some chemical constituents to potentially require remediation and/or curtailment of the constituent input to the waterbody. However, many aquatic sediments are naturally toxic to some forms of aquatic life under the toxicity tests used and yet have high quality sport fisheries in the overlying waters. This paper addresses the issues that need to be considered in evaluating the results of a sediment quality assessment procedure, such as exceedance of an SQC value and/or have aquatic life toxicity under laboratory test conditions, in order to determine whether the toxicity or excessive concentration found is a potentially significant cause of real water quality deterioration in the waterbody of concern. Also addressed is the reliability of some of the sediment quality assessment procedures used such as chemically based estimates of toxicity compared to direct toxicity measurements.

Key words: sediment quality, water quality, toxicity, sediment quality criteria

**INTRODUCTION**

Beginning in the early 1970's attention began to be focused on the water quality significance of chemical constituents present in aquatic sediments. At that time it was beginning to be more widely recognized that aquatic sediments near urban/industrial areas contained elevated concentrations of chemicals that at some locations and situations were adverse to water quality. It was assumed then without evaluation that increased sediment concentrations of chemical constituents such as heavy metals, chlorinated hydrocarbon pesticides and nitrogen and phosphorus compounds and other chemicals would be adverse to aquatic life, increase eutrophication, result in increased bioaccumulation of hazardous chemicals such as mercury and/or chlorinated hydrocarbons in fish to cause the organisms to represent a perceived increased human health hazard when used as food.

**REGULATING CHEMICAL CONSTITUENTS IN DREDGED SEDIMENTS**

The initial focus of regulatory attention for chemically contaminated sediments was the Corps of Engineers (US COE) maintenance dredging of harbors, navigation channels, etc. The US COE dredges about  $400 \times 10^6$

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yds<sup>3</sup>/year of US waterway sediments. About 10% of this dredging occurs with sediments that have elevated concentrations of several chemical constituents that are potential pollutants. These sediments are typically found near urban, industrial areas which include many US harbors and navigation channels.

In the early 1970's, the Federal Water Quality Administration (FWQA), a predecessor organization of the US EPA, developed the Jensen criteria to determine if excessive concentrations of selected chemicals (zinc) or chemical characteristics (COD, volatile solids) existed in a sediment that was to be dredged (Boyd *et al.* 1972). Typically at that time, dredged sediment disposal occurred by the least expensive method available which usually involved open, deeper water disposal. The adoption of the Jensen criteria required that alternative, typically more expensive methods such as on land disposal, be used if the concentration of the Jensen criteria parameters were exceeded. It was assumed by the FWQA at that time, without evaluation, that the so-called confined on land disposal was less damaging to the environment than the less expensive open water disposal due to the presence of chemicals in the sediments. It has subsequently been found that on land disposal of contaminated dredged sediments can be significantly adverse to the environment.

Lee and Jones (1992a), Lee and Jones-Lee (1994a) and Wright (1992) have reviewed the water quality aspects of dredging and dredged sediment disposal. As they discuss, the US COE conducted a \$30 million, five year research program (Dredged Material Research Program - DMRP) during the mid 1970's specifically devoted to evaluating the water quality significance of dredging and open water disposal of aquatic sediments containing elevated concentrations of a variety of constituents that are potentially adverse to water quality. The results of the DMRP conclusively showed what was known in the late 1960's, that total concentrations of a chemical constituent in aquatic sediments is not a reliable basis for assessing water quality impacts, such as toxicity, bioaccumulation, etc., of these constituents.

This led the US EPA and COE to develop biological effects-based sediment quality evaluation approaches for assessing the water quality significance of potential pollutants in a waterway sediment that was to be dredged and disposed by open water disposal (US EPA/COE 1991, 1994). The biological effects-based approaches adopted by the US EPA and COE focuses on directly measuring aquatic life toxicity in a sediment using sensitive forms of aquatic life rather than trying to estimate toxicity based on chemical concentrations present in the sediment. As discussed by Lee and Jones-Lee (1993a), the aqueous environmental chemistry of constituents in sediments is such that it is not possible to reliably estimate toxicity for potentially toxic chemicals based on their concentrations in sediments. The basic problems with trying to use chemically-based approaches is that concentrations in sediments typically expressed as mg constituent/kg sediment (dry weight) do not have the same meaning as concentrations in water, mg/L (kg of water). The sediment matrix is of variable composition (sand, clay, organics, shell) and since the detoxification-binding ability of sediments for chemical constituents is a function of this matrix, the composition of the matrix is the important factor in determining whether a potentially toxic constituent in sediments, such as a heavy metal, is in fact toxic in a particular sediment. The US EPA and COE biological effects-based approaches have been proven to be reliable for assessing potentially significant problems associated with the open water disposal of contaminated dredged sediments. These assessment approaches provide a technical base upon which to evaluate whether chemical constituents in sediments represent significant causes of water quality/beneficial use impairment of waterbodies.

#### DEVELOPMENT OF SEDIMENT QUALITY CRITERIA

In the mid-1980's, the US EPA began to develop sediment quality criteria (SQC). This effort was in response to the finding that aquatic sediments in many parts of the US have accumulated significantly elevated concentrations of a variety of chemical constituents that represent a potential threat to the designated beneficial uses of the overlying and nearby waters. There was and still is need for a reliable evaluation assessment approach for determining whether a sediment contains sufficient concentrations of a toxic-bioavailable chemical to be significantly adverse to the designated beneficial uses of the waterbody in which the sediments are located.

Equilibrium Partitioning Based Criteria. The Agency's SQC development efforts were designed to parallel the Agency's water quality criteria where numeric chemical specific values would be used to determine the excessive

concentrations of a constituent in sediments that could require remediation and/or altered NPDES permitted discharge limits for those constituents in wastewater discharges and stormwater runoff that tend to accumulate in aquatic sediments in excess of the SQC value. Throughout the 1990's, the US EPA has been struggling with trying to develop reliable SQC. The Agency attempted to circumvent the inherent fundamental deficiencies of chemical concentration-based assessment approaches by normalizing these concentrations based on one of the factors of the bulk sediment matrix that influence the toxicity availability of constituents. Agency as well as other research has demonstrated that the toxic-available form of chemical constituents present in the sediment is the dissolved form present in the interstitial waters. In an overly simplistic approach, the Agency assumed that the dissolved form for certain organics (some PAH's and chlorinated pesticides) could be estimated based on an equilibrium partitioning model involving the particulate organic carbon present in the sediments (US EPA 1993a,b).

In order to estimate the dissolved forms of certain heavy metals in the sediment interstitial water, it was assumed that the concentration of the dissolved form was only controlled by metal sulfide precipitates, and that all dissolved forms of metals in interstitial waters are in toxic-available forms (US EPA 1994). As discussed by Lee and Jones-Lee (1993a, 1994b), the Agency's draft criteria development approach and draft criteria have been found by several reviewing agencies, entities and individuals to be an inappropriate basis for developing numeric chemical specific criteria that could be used in the regulatory arena to determine excessive concentrations of chemical constituents in sediments.

The fundamental problem with the US EPA's approach is that exceedance of a proposed sediment quality criterion does not necessarily mean that the chemical constituent of concern in the sediments is contributing dissolved forms of the constituent to the interstitial waters that are toxic-available to aquatic life associated with the sediments. The Agency's overly simplistic two component box model used to develop the equilibrium partitioning estimates of dissolved forms ignores a wide variety of factors that could influence the concentrations of constituents in interstitial waters that are adverse to aquatic life. Fundamentally, the chemically-based SQC's can never be used as a stand alone criterion. They will always have to be backed by toxicity measurements.

Since the measurement of aquatic life toxicity is the objective of the SQC values, it makes little sense to estimate toxicity when well established, reliable procedures have been used for years by the Agency and the COE to directly measure toxicity to aquatic life in aquatic sediments. It is for this reason that the authors and many others (Lee and Jones-Lee 1993a, Wright 1992) recommend basing sediment quality criteria on direct toxicity testing and not to attempt to indirectly estimate toxicity based on sediment quality criteria approaches such as those which the Agency is in the process of trying to develop. While the Agency proposed these sediment quality criteria in 1993, they have still not finalized these criteria because of wide-spread opposition to them based on their lack of technical validity as a regulatory basis for determining excessive concentrations of chemical constituents in sediments.

Co-occurrence Based Sediment Quality Assessment Approaches. Long and Morgan (1990) compiled information from the literature on the concentrations of constituents found in sediments and what the literature author(s) reported was an impact on sediment associated aquatic life such as toxicity, altered organism assemblages, etc. This data was compiled in increasing concentration for each chemical parameter considered, and certain statistical characteristics of the data were developed as to whether a particular concentration of a constituent had been found in any sediment that was included in the database to be associated with (co-occurred with) a perceived adverse impact. This has led to what has become known as co-occurrence-based sediment quality criteria-assessment. The apparent effects threshold approach (AET) is also a co-occurrence-based approach that suffers from the same fundamental technical deficiencies as the Long and Morgan co-occurrence-based approach.

There was no attempt by Long and Morgan to develop any cause and effect between the concentrations of constituents in the sediments and the so-called effect that was noted. In compiling their data, Long and Morgan chose to leave out of the database some of the most important causes of toxicity such as low dissolved oxygen, ammonia and hydrogen sulfide. There is little doubt that much of the so-called adverse impacts reported by Long and Morgan were in fact due to these chemicals and were not due to the constituents in the ranked tables of concentrations developed by them.

Subsequently, other individuals such as MacDonald (1992) and Long *et al.* (1995) have expanded on the original Long and Morgan database. They claim that the co-occurrence based approaches have reliable predictive capability in assessing whether a sediment would be toxic to a particular chemical based on whether the concentration of that chemical in the sediment exceeds a certain statistically derived "effects" concentration. However, a critical review of the Long and Morgan, MacDonald and Long *et al.* co-occurrence based approaches shows that it is fundamentally flawed, since it is based on the total concentrations of a chemical constituent in sediments independent of whether the constituent is in a toxic-available form. Further, the statistical characteristics of the database used in developing the "effects" value is not based on cause and effect and, in fact, has no valid technical base.

In addition, as discussed by Lee and Jones-Lee (1996a,b,c) a number of groups and individuals have critically examined the reliability of Long and Morgan co-occurrence based values for predicting sediment toxicity and have found that they are not reliable. Unfortunately, some groups within the US EPA and other groups have adopted co-occurrence based values as a basis for estimating excessive concentrations of chemical constituents in aquatic sediments. While some of those responsible for following this approach state that they understand the lack of technical validity of co-occurrence based values, they proceed with their use under the premise that this is "the only information available" on how to utilize the chemical concentration data that exists for aquatic sediments. Obviously, this is flawed reasoning where those who are following this approach are asserting that it is better to have some estimate of sediment toxicity, even though it is unreliable, than no estimate. This is more of the numeric chemical approach where regulators, environmentalists and others simply want a numeric value independent of its reliability as a basis in order that they can "regulate."

It is the authors' position that it is better to have no estimate of sediment toxicity than to use what is obviously a fundamentally flawed approach for estimating sediment toxicity such as co-occurrence-based values. With no estimate of toxicity, it would then be possible to obtain the funds needed to develop the necessary toxicity data. Under the current approach, those responsible for controlling funds needed to properly measure toxicity are lulled into believing that the co-occurrence, or for that matter the equilibrium partitioning based approaches are sufficiently reliable so that the regulatory process can proceed without actually reliably determining whether the sediments are, in fact, toxic.

SQC's and Co-occurrence Effects for Sediment Quality Screening. There are some who advocate (see Adams 1993, US EPA 1994 and many others who utilize the co-occurrence based approaches) that equilibrium partitioning based or co-occurrence based sediment quality criteria can be used to "screen" sediments for potential adverse impacts. However, as Lee and Jones-Lee (1993b, 1995, 1996c) point out, in the regulatory arena that exists today sediment quality screening procedures must be reliable, otherwise dischargers and the public may be trapped into inappropriate regulatory approaches for sediment remediation and NPDES discharge limit changes that are not based on technically valid assessments of real water quality impairments.

Regulatory agencies and some others attempt to develop single-value numeric values for integrating the toxic responses of reference sites, test sites, different types of test organisms, etc. Approaches such as computing the geometric mean of the difference between the reference toxicity and test site toxicity for different organisms, while enabling the regulators to develop a single numeric value which may serve as a basis for regulation, this approach is obviously not valid and does not properly reflect the real world of sediment toxicity that must be considered in developing meaningful assessments of toxicity as part of a technically valid regulatory program.

The basic problems with trying to use chemically-based approaches is that concentrations in sediments typically expressed as mg constituent/kg sediment (dry weight) do not have the same meaning as concentrations in water, mg/L (kg of water). The sediment matrix is of variable composition (sand, clay, organics, shell, etc.) and since the detoxification-binding ability of sediments for chemical constituents is a function of this matrix, the composition of the matrix is the important factor in determining whether a potentially toxic constituent in sediments, such as a heavy metal, is in fact toxic in a particular sediment.

Bioaccumulation. It is generally understood today that the coupling between available forms of chemical constituents in sediments and the bioaccumulation of these constituents in edible forms of aquatic life of importance for use as food by humans or for wildlife is poorly understood. At this time it is not possible to predict with any degree of reliability the actual bioaccumulation levels that will occur in desirable forms of aquatic life that are used as human food. While chemical partitioning models are fairly reliable in predicting bioaccumulation under aquarium-like conditions for many chemical constituents which partition between a sediment organic carbon and fatty tissues in fish, in the real world where bioaccumulation occurs and is of concern, the simple partitioning models or aquarium tests are not adequate to predict the actual levels of accumulation that will occur. In general, they tend to significantly overestimate bioaccumulation. At this time, the only reliable way to estimate whether excessive bioaccumulation will occur is to measure the actual accumulation that occurs within fish and other edible aquatic organism tissue of concern to the public as food.

#### APPROPRIATE ASSESSMENT OF SEDIMENT TOXICITY

The assessment of sediment toxicity as part of the development and implementation of a sediment based water quality management program is becoming recognized as a far more complex issue than simply testing a sediment for toxicity to a single organism. Further, because of the inherent unreliability of chemically based estimates of sediment toxicity, it is necessary to directly assess the toxicity of sediments using a suite of sensitive test organisms. Where multiple sensitive species are used for sediment toxicity testing, significantly different responses are being found among different types of aquatic organisms to toxicants in sediments. It is inappropriate to rely only on the toxic response of one organism, as is sometimes done. At least two, and preferably three, sensitive forms of aquatic life should be used to assess toxicity as part of evaluating whether there is real significant toxicity in a sediment. In conducting such tests as part of a sediment quality regulatory program, there are a number of issues that need to be considered in interpretation of the test results. This section reviews some of these issues.

Non-Chemically Caused "Toxicity." A variety of factors other than toxicants cause toxic responses in organisms that are being used to assess the toxicity of both reference sites and test sites. At this time, there is a poor understanding of how these factors influence toxicity test results for a number of organisms. One of the most well-known of these factors is the impact of sediment grain size on *Rhepoxynius abronius* survival. As further sediment toxicity work is done with a variety of sensitive test organisms, the other so-called "toxic" effects will become better recognized and eventually understood.

Natural vs. Anthropogenically Caused Sediment Toxicity. Many aquatic sediments below the few millimeter thick surface layer are naturally toxic to many forms of aquatic life. This natural toxicity arises from the settling of algae that grow in the overlying waters. The algae serve as a source of biochemical oxygen demand which, when incorporated into the sediments, reduces the oxygen levels to zero. This in turn sets off a series of biochemical and chemical reactions leading to the accumulation of a number of reduced-chemical species. Of primary importance are ferrous iron and various sulfide species. These chemicals can accumulate to thousands of milligrams per kilogram of sediment and thereby serve as an important source of oxygen demand that immediately reacts with any oxygen that diffuses into the sediments.

While the depletion of dissolved oxygen and production of hydrogen sulfide and ammonia occurs naturally in many sediments associated with the natural fluxes of aquatic plant nutrients, the activities of man in a waterbody's watershed can significantly increase the flux of nutrients (N and P) to a waterbody and thereby increase the oxygen demand of the sediments through the biochemical respiration of the dead algae that develop in the overlying waters. In the 1960's and 1970's, considerable attention was given to the excessive fertilization of waterbodies caused by the introduction of aquatic plant nutrients. Lee (1973), published a review on this topic. Rast and Lee (1983) have provided guidance on estimating nutrient loads to waterbodies based on land use in the waterbodies' watershed.

In some waterbodies, such as lakes, estuaries, slow-moving rivers, etc., the oxygen demand exerted by the algae is sufficient to deplete oxygen levels at the sediment-water interface. In some cases, such as many eutrophic lakes, there is a complete depletion of oxygen, and toxic levels of hydrogen sulfide accumulate in the hypolimnion.

Therefore, any oxygen obligate organisms that inhabit the sediments of such waterbodies are killed because of low DO, high sulfide, and, in some cases, elevated ammonia.

Eutrophic waterbodies where substantial areas of sediments are toxic to aquatic life are well-known to produce highly desirable warm water sports fisheries. If the temperature of the surface waters stays below about 20°C, these waterbodies can maintain highly desirable cold water sports fisheries as well. Therefore, the presence of highly toxic conditions in sediments from natural causes, which decimates the benthic organism populations for a considerable part of the year, does not preclude the presence of an outstanding sports fishery. This is an issue that must be better understood and considered in assessing the need for sediment remediation to control aquatic life toxicity, since the presence of sediment toxicity does not preclude high value aquatic life resources.

Sensitivity of Test Organisms to Ammonia Toxicity. Another aspect of the current approach toward assessing the significance of sediment toxicity that is poorly justified is the emphasis on toxicity that is measured by certain test organisms such as some of the amphipods, which are not particularly sensitive to ammonia toxicity. One of the organisms that is often used to assess sediment toxicity is *Rhepoxynius abronius*, which is at least a factor of 10 to 20 times less sensitive to ammonia toxicity than many fish and shellfish larvae, which represent, from a public perspective, more important organisms than the test organism. Some are choosing to ignore natural and anthropogenically derived toxicity associated with the input of aquatic plant nutrients. To require the remediation of toxicity associated with chemicals that *Rhepoxynius* is particularly sensitive to, but disregard the toxicity that is of importance to other organisms more directly linked to aquatic organisms of concern to man is questionable. It makes little difference to an oyster or fish larvae whether it is killed by ammonia derived from natural or anthropogenically derived nutrients that lead to algae/low DO or by a heavy metal or PAH. Jones-Lee and Lee (1993) have reviewed the occurrence and water quality significance of ammonia as a sediment toxicant. Their review should be consulted for further information.

The issue of natural or nutrient caused toxicity versus heavy metal or organic toxicity needs to be better understood and properly considered in evaluating the need for sediment remediation and NPDES permit changes based on aquatic life toxicity to a particular test organism that is not necessarily an organism that the public would consider to be a key organism in aquatic sediments for maintenance of the desirable forms of aquatic life. The issue of primary concern is whether the public either directly or indirectly should spend large amounts of money remediating contaminated sediments or paying for increased treatment of point and non-point source discharges and runoff because a particular test organism shows a toxic response under the conditions of the laboratory test that is used.

There seems to be considerable support for controlling toxicity that is associated with toxicants that kill highly desirable forms of aquatic life of interest to the public, such as fish and shellfish larvae. There may be limited support for controlling toxicity that is of importance only to certain types of benthic or epibenthic organisms that are not necessarily key components of the food web. This does not mean that they do not play a role in the food web; the question is whether their reduced numbers or absence would be significantly adverse to desirable forms of aquatic life of interest to the public. There is need to better understand the water quality significance of various types of aquatic organisms that are used as test organisms for assessing aquatic life toxicity, and what toxicity to them means to the beneficial uses of a waterbody.

There are some who advocate the removal of ammonia from the sediment by raising the pH and airstripping and then lowering the pH to its original conditions as a means of assessing the toxicity of the anthropogenically derived Priority Pollutants. They consider the ammonia toxicity an interference in the toxicity test. It is important to understand, however, as discussed herein, that ammonia derived from algae that develop in a waterbody is also a potentially significant anthropogenically derived constituent arising from the fertilization of the waterbody by aquatic plant nutrients, which in turn stimulate algal growth and lead to increased ammonia concentrations in sediments.

There is need to more critically consider the significance of nutrient-derived toxicity in formulating toxic control programs than is occurring today. This is especially important because of the fact that the nutrient-derived

toxicity (i.e. aquatic plant nutrients, algal growth and decay, dissolved oxygen depletion and ammonia and hydrogen sulfide generation) is one of the most important, if not the most important cause of toxicity in aquatic sediments. Latimer (1992), in a review of the US EPA EMAP studies along the east coast of the US, reported that the most common cause of toxicity in east coast nearshore marine sediments is low-dissolved oxygen. While ammonia and hydrogen sulfide were not measured in the initial EMAP studies, they would be expected to be present in the areas of low DO.

Selecting Reference Site. Current approaches for assessing the toxicity of chemical constituents in test site sediments involve measuring the toxicity of a sediment sample(s) relative to the toxicity of another area (reference site). A reference site is supposed to be non-impacted by anthropogenically derived constituents and have the same physical, chemical and biological characteristics as the test site. As more information is gained on the toxicity of so-called reference sites, it is being found that the selection of an appropriate reference sediment is difficult to achieve. One of the primary problems is that some of the "non-polluted" sediments show toxicity to some test organisms. This toxicity is not necessarily consistently present in the particular reference site. Based on the results of the State of California unpublished BPTCP testing of sediments in the San Francisco Bay region, it appears that toxicity in some reference sediments occurs only at certain times of the year. Whether this toxicity is due to some unknown anthropogenically derived constituent or due to natural conditions, such as the decay products of algae or other forms of aquatic life, is not known at this time.

Toxicity in reference sites greatly complicates the determination of the level of toxicity in a test sediment, since it is not known whether the test sediment shows the same natural background toxicity as the toxicity found in the reference sediments. It is for this reason that a suite of test organisms must be used on the reference site as with the test site, and a suite of so-called reference sites should be used to determine whether there is potentially significant toxicity in a particular sediment.

Reliability of Chemically Based Estimated Toxicity. There are some who, as a way of simplifying the assessment of toxicity, advocate the use of chemical testing as a basis for "determining" whether sediments are potentially toxic, by the US EPA's equilibrium partitioning approach. As discussed herein, such an approach is not technically valid for a variety of reasons, including that it assumes that the organisms used to determine the toxicity associated with the chemicals that were used to develop the water quality criterion which is being used to judge whether a sediment is toxic based on "predicted" excessive dissolved concentrations in the interstitial waters is representative of the toxicity that would occur for benthic and epibenthic organisms of concern in a particular sediment. If a suite of sensitive test organisms shows a significantly different toxicity in the testing of a particular sediment, then it is likely that there will also be a difference between the sensitivity of the water column organisms used to develop the water quality criterion and the benthic organisms used in toxicity tests. This issue needs to be more carefully evaluated than has been done to date before it can be assumed that this assumption is appropriate.

#### INTERPRETATION OF THE WATER QUALITY SIGNIFICANCE OF SEDIMENT TOXICITY

Once a reliable assessment of the toxicity of the sediments in the area of concern has been developed, then the task of evaluating the significance of this toxicity as it may impact the designated beneficial uses of the waterbody should be undertaken. This is a neglected area that needs attention if technically valid, cost effective sediment quality management programs are to be implemented. At the present time, the focus of regulatory agencies is largely that of determining whether there is a statistically significant difference in the toxicity measured under laboratory conditions between a test site and a reference site. Where such differences are found it is often assumed that such a difference represents a significant adverse impact on water quality and therefore could require remediation and NPDES permit alteration. It is, however, clear that statistically significant differences in toxicity between a test site and a reference site do not necessarily mean that test site sediment toxicity is of water quality significance.

The fact that many waterbodies have naturally toxic sediments, yet have outstanding fisheries and other aquatic life resources means that sediment toxicity does not necessarily significantly impair the designated beneficial uses of a waterbody. At this time the coupling between sediment toxicity and water quality/use impairment of

concern to the public is poorly understood. It is certainly not, however, a one-to-one coupling where any sediment toxicity measured under laboratory conditions represents a significant impairment of beneficial uses of a waterbody.

The issue that must be addressed is what do the laboratory toxicity test results mean to the designated beneficial uses of the waterbody of potential concern to the public, who must ultimately either directly or indirectly pay for sediment remediation and chemical constituent control programs in point and non-point source discharges. The public is typically concerned about the numbers, types and characteristics of desirable aquatic organisms. Fish, shellfish, waterfowl and wildlife that are utilized as food are the focal points of concern. It is the author's finding that the public has little concern for the numbers and types of benthic worms or other organisms that are not significant to the forms of aquatic life of concern to the public. In times of highly restricted funding it is appropriate to evaluate whether the public should pay large amounts of money to remediate a contaminated sediment because the contaminant causes aquatic life toxicity which is of little or no importance to the numbers, types and characteristics of desirable forms of aquatic life in the waterbody of concern or those associated with it.

In 1972 Congress, as part of developing what became the Clean Water Act, concluded that there were unlimited financial resources available to control water pollution. At that same time, Congress based the nation's water pollution control programs on protecting designated beneficial uses of the nation's waters. Today, while it is now recognized that there are not unlimited financial resources available to control water pollution, the nation's water pollution control programs are still focused on protecting and, where degraded, enhancing the designated beneficial uses of waterbodies.

As pointed out by Lee and Jones (1992b) when the US EPA began to propose sediment quality criteria, the coupling between sediment toxicity and water quality issues of importance to the public must be defined. Thus far the US EPA and other regulatory agencies have failed to adequately address this issue. Without formulating an appropriate policy on this issue, it is highly likely that significant overregulation and substantial waste of public and private funds can occur in sediment remediation programs. The US EPA, other governmental agencies, the regulated community and the public need to convene an expert panel of individuals knowledgeable in water quality issues to formulate an approach that could be used to determine, on a site-specific basis, whether sediment toxicity represents a significant adverse impact on the beneficial uses of a waterbody that should require remediation.

The reliability of the proposed approach for coupling sediment toxicity to water quality use impairment impact should be evaluated at a number of locations. Eventually, from this approach, it will be possible to provide guidance to state and local regulatory agencies on how to determine whether the toxicity found in a particular sediment is of such significance to water quality/use impairment as to require remediation and control.

**BPI Weight-of-Evidence Approach.** A variety of approaches have been proposed to determine whether the chemical constituents in sediments are of such water quality significance as to require remediation and/or source reduction. Often, attempts are made to simplify the decision making process by developing arbitrary numeric weighting of various factors that are considered to be of some importance in developing a regulatory approach for sediment quality evaluation and management. An extreme example of such an approach was the State of California Water Resources Control Board Bay Protection and Toxic Cleanup Program designation of "toxic hot spots." The State Water Resources Control Board staff (WRCB 1995) contrived an elaborate approach of numeric ranking that included a variety of factors for designating toxic hot spots. However, upon review by professionals knowledgeable in the topic area, the approach was found to be technically invalid and was abandoned by the WRCB.

#### RECOMMENDED SEDIMENT QUALITY EVALUATION APPROACH

There is widespread, growing recognition that a non-numeric, best professional judgment (BPJ) approach should be used to evaluate the water quality significance of chemical constituents and/or toxicity in aquatic sediments. A properly conducted BPJ sediment quality weight-of-evidence evaluation involves the following:

- The use of a BPJ integrated assessment of the aquatic life toxicity test results.
- Assessment of excessive bioaccumulation of hazardous chemicals in edible aquatic organism tissue and the whole organism in excess of the concentrations that are considered hazardous for human health and wildlife



- use of the organisms as food.
- Appropriately used chemical characteristics of the sediments and associated waters.
- Aquatic organism assemblages present in the sediments of concern relative to the aquatic organisms' habitat characteristics.

The BPJ should be conducted by a panel of experts who represent the interests of those concerned with sediment quality in a region. Efforts should be made to try to exclude significant political or other influences on the BPJ deliberations. Some of the issues that need to be considered in developing a technically valid weight-of-evidence approach are summarized below.

**Assessment of Toxicity.** The assessment of toxicity should be based on the measurement of toxicity in representative sediment samples relative to appropriately selected reference sites. At least two, and preferably three, reference sites should be used. Further, at least two, and preferably three, sensitive test organisms should be used in the toxicity assessment. Toxicity should be measured preferably quarterly over at least a period of one year. Toxicity assessment should consider issues such as natural or anthropogenically derived toxicity associated with low dissolved oxygen, hydrogen sulfide and ammonia. The areal extent of toxicity should be assessed in terms of the area and depth in sediments.

If there is sufficient toxicity found to potentially significantly adversely impact the beneficial uses of the waterbody, an effort should be made to determine the cause of the toxicity through a carefully conducted screening toxicity investigation evaluation (TIE). It is important to note, however, that it is not necessary to identify the chemical constituents responsible for toxicity in order to effect a toxicity control program. Sediment toxicity can readily be due to unregulated chemicals that will not be identified in the TIE. The failure to identify the cause of the toxicity is not a reason not to control its impacts and its sources. Toxicity testing can be used in the forensic approach to determine the source of the toxicity, i.e. are current discharges or runoff contributing substances that can accumulate in the sediments and cause toxicity. It is important in conducting such testing programs to adequately consider the aqueous environmental chemistry of constituents in identifying the cause and source of toxicity. The toxicity testing procedures used by the US EPA/COE 1991, 1994, as well as other adequately evaluated procedures, can be used for testing toxicity.

**Bioaccumulation.** The approach to assess whether chemical constituents in sediments are a source of excessive bioaccumulation is first to determine whether the waters of concern associated with the sediments do in fact have aquatic life with excessive bioaccumulated constituents of concern that are potentially derived from sediments. If the fish and other forms of aquatic life do not have excessive concentrations of the hazardous bioaccumulatable chemicals, then there is no bioaccumulation problem that needs to be considered from a human health perspective. However, consideration must also be given to higher trophic level wildlife, such as birds and animals that utilize fish and aquatic life as food in evaluating the potential significance of bioaccumulation. The water quality management field is just beginning to develop wildlife protection criteria which appropriately consider whether chemical constituents in water and sediments are bioaccumulating to a sufficient extent in wildlife food to be adverse to the wildlife.

If excessive bioaccumulation is occurring, then studies need to be conducted to determine whether the sediments in a particular region are a potential source of the constituents responsible for the excessive bioaccumulation. The US EPA Corps of Engineers' approach can estimate the potential for bioaccumulation of some constituents (US EPA/COE 1991). If it is suspected that the sediments are a significant source of bioaccumulatable constituents in higher trophic level organisms, then site-specific studies should be conducted using laboratory and field caged organisms to estimate whether the actual transfer of constituents from sediments to higher trophic level organisms is occurring.

**Appropriate Use of Chemical Data.** As discussed herein, great caution must be exercised in utilization of chemical data in assessing the water quality significance of chemical constituents in aquatic sediments. Aquatic sediments are highly complex chemical systems where a wide variety of reactions occur that tend to detoxify potential toxicants, such as heavy metals, pesticides, PAH's, etc. Far too often, attempts are made to utilize chemical concentration data as a basis for estimating water quality impacts. As discussed in the supplemental appendix to

this paper and in references cited in the reference list, such approaches have thus far largely proven to be highly unreliable.

Total concentrations of constituents, metal sulfide or organic TOC normalized constituent concentrations, co-occurrence based "effect" values, AET's and similar approaches are not reliable values for assessing water quality impacts of chemical constituents in aquatic sediments. Total concentration based Long and Morgan, McDonald and AET values have no valid role in a properly conducted weight-of-evidence approach. They provide highly inaccurate assessments of the potential water quality significance of constituents in sediments and should not be used for any purpose.

There are situations where acid volatile sulfides above the sum of the heavy metals can be useful to rule out metals as a cause of toxicity. Similarly, TOC normalized sediment concentrations for some constituents can be used as a component of a TIE to eliminate from further consideration the potential significance of certain organics as a cause of toxicity. The reverse, however, is not reliable; these approaches cannot predict toxicity. Basically, the appropriate approach to follow in utilizing chemical information in a weight-of-evidence approach is through a properly conducted TIE investigation where coordinated sediment fractionation/toxicity testing is undertaken to determine the chemical fractions in sediments that are responsible for the toxicity.

Organism Assemblages. As part of developing a sediment quality remediation program designed to control aquatic life toxicity, it is important to determine the numbers, types and characteristics of aquatic organisms in the region of concern compared to several appropriate reference sites which have the same physical, chemical and biological characteristics. These determinations should be made at least twice during the year. Once in the late winter/spring and then again in the late summer/fall period in order to detect the seasonal effects on organism populations.

## SUMMARY

From the information available, many of the chemical constituents of concern in aquatic sediments are of concern because of potential toxicity to aquatic life or higher trophic level organisms. Many aquatic sediments show aquatic life toxicity due to natural, and in some cases, anthropogenically derived chemicals either directly, through the presence of heavy metals and organics, or indirectly, through nutrient stimulation of algal or other aquatic plant growth which then through the decay of these plants leads to oxygen depletion in sediments and the associated toxicity due to low DO and the concomitant development of ammonia and hydrogen sulfide. Both ammonia and hydrogen sulfide are highly toxic to many forms of aquatic life.

While attempts are made to estimate toxicity based on chemical concentrations and relationships developed in co-occurrence based approaches or equilibrium partitioning based sediment quality criteria, it is readily apparent that these approaches are not technically valid. The only reliable approach for assessing sediment toxicity is to directly measure toxicity using a suite of sensitive organisms. These measurements should include measurements of the test sediment as well as reference sediment(s) made several times during a year.

The approach that should be used to assess whether the sediment is toxic involves a best professional judgement (BPI) integration of the toxicity and other information on the characteristics of the area. Attempts to assess whether sediments are toxic with less than this amount of information can readily prove to be highly unreliable and provide an inadequate base of technical information upon which to develop a regulatory program for sediment quality management.

## REFERENCES

- Adams, W.J. (1993) "Sediment Quality Criteria." authors reply, *Environ. Sci. Technol.*, 27, 205-206.
- Boyd, M.B., Saucier, P.T., Keeley, J.W., Montgomery, R.L., Brown, R.D., Mathis, D.B., Guice, C.J. (1972) "Disposal of Dredge Spoil. Problems Identification and Assessment and Research Program Development." Technical Report 11-72-8, US Army Corps of Engineers Waterways Experiment Station, Vicksburg, MS.

- Jones-Lee, A., and Lee, G.F. (1993) "Potential Significance of Ammonia as a Toxicant in Aquatic Sediments." *Proc. First International Specialized Conference on Contaminated Aquatic Sediments: Historical Records, Environmental Impact, and Remediation*, International Assoc. Water Quality, London, England, pp 223-232.
- Latimer, R. (1992) "The Extent and Severity of Sediment Contamination in the Estuaries of the Mid-Atlantic Region." Presented at US EPA Forum on the Extent and Severity of Sediment Contamination, Chicago, IL.
- Lee, G.F. (1973) "Eutrophication." *Transactions of the Northeast Fish and Wildlife Conference*, pp 39-60.
- Lee, G.F., and Jones, R.A. (1992a) "Water Quality Aspects of Dredging and Dredged Sediment Disposal." IN: Handbook of Dredging Engineering, Herbich, J. (ed), McGraw-Hill, NY, pp 9-23 - 9-59.
- Lee, G.F., and Jones, R.A. (1992b) "Sediment Quality Criteria Development: Problems with Current Approaches." Workshop notes, 1992 National R & D Conference on the Control of Hazardous Materials, Hazardous Materials Control Research Institute, Greenbelt, MD, 120pp.
- Lee, G.F., and Jones-Lee, A. (1993a) "Sediment Quality Criteria: Numeric Chemical- vs. Biological- Effects-Based Approaches." *Proc Water Environment Federation Natl. Conf., Surface Water Quality & Ecology*, 389-400.
- Lee, G.F., and Jones-Lee, A. (1993b) "Sediment Quality Criteria (SQC's) for Screening Sediments for Toxicity," *Environ. Sci. Technol.* 27, (6), 994.
- Lee, G.F., and Jones-Lee, A. (1994a) "Contaminated Dredged Sediment Disposal Criteria," IN: Dredging '94: Proceedings of the Second International Conference on Dredging and Dredged Material Placement, American Society of Civil Engineers, NY, pp 121-130.
- Lee, G.F., and Jones-Lee, A. (1994b) "Comments on US EPA Proposed Sediment Quality Criteria Based on Acid Volatile Sulfide Normalization Heavy Metal Data," Submitted to the Science Advisory Board Sediment Criteria Subcommittee, Washington, DC.
- Lee, G.F., and Jones-Lee, A. (1995) "Appropriate Use of Numeric Chemical Concentration-Based Water Quality Criteria." *Human and Ecological Risk Assessment*, 1, (1), 5-11.
- Lee, G.F., and Jones-Lee, A. (1996a) "'Co-Occurrence' in Sediment Quality Assessment." Submitted for publication.
- Lee, G.F., and Jones-Lee, A. (1996b) "Can Chemically Based Sediment Quality Criteria Be Used as Reliable Screening Tools for Water Quality Impacts?" *Society for Environmental Toxicology and Chemistry, SETAC News Learned Discourses*, 16, (3), 14-15.
- Lee, G.F., and Jones-Lee, A. (1996c) "Appropriate Use of Numeric Chemical Concentration-Based Water Quality Criteria: Supplemental Discussion." *Human and Ecological Risk Assessment*, 2, (2), 233-234.
- Long, E., and Morgan, L. (1990) "The Potential for Biological Effects of Sediment-Sorbed Contaminants Tested in the National Status and Trends Program." NOAA Technical Memorandum NOS OMA 52, NOAA, Seattle, WA.
- Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D. (1995) "Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments." *Environ. Manag.* 19, 81-97.
- MacDonald, D. (1992) "Development of an Approach to the assessment of Sediment Quality in Florida Coastal Waters." Report to Florida Department of Environmental Regulation, Tallahassee, FL.

Rast, W., and Lee, G.F. (1983) "Nutrient Loading Estimates for Lakes." *J. Environ. Engr. Div. ASCE* 109, 502-517. See also closure discussion, (1984) "Nutrient Estimates for Lakes." *Journ. Environ. Engrg.* 110, 722-724.

US Environmental Protection Agency (1993a) "Sediment Quality Criteria for the Protection of Benthic Organisms." Acenaphthene: EPA-822/R-93-013, pp 94; Dieldrin: EPA-822/R-93-015, pp 102; Endrin: EPA-822/R-93-016, pp 104; Fluoranthene: EPA-822/R-93-012, pp 102; Phenanthrene: EPA-822/R-93-014, pp 88, US EPA Office of Water, Washington, DC.

US Environmental Protection Agency (1993b) "Technical Basis for Deriving Sediment Quality Criteria for Nonionic Organic Contaminants for the Protection of Benthic organisms by Using Equilibrium Partitioning." US EPA Office of Water, EPA-822/R-93-011, pp 68, Washington, DC.

US Environmental Protection Agency (1994) "Briefing Report to the EPA Science Advisory Board on the Equilibrium Partitioning Approach to Predicting Metal Bioavailability in Sediments and the Derivation of Sediment Quality Criteria for Metals-Vol I." US EPA Office of Water, EPA-822/D-94-002, pp 306, Washington, DC.

US Environmental Protection Agency/US Army Corps of Engineers (1991) "Evaluation of Dredged Material Proposed for Ocean Disposal-Testing Manual." US EPA Office of Water, EPA-503/8-91/001, Washington, DC.

US Environmental Protection Agency/US Army Corps of Engineers (1994) "Evaluation of Dredged Material Proposed for Discharge in Waters of the US-Testing Manual (Draft)." US EPA Office of Water, EPA-823-B-94-002, Washington, DC.

WRCB (1995) Functional Equivalent Document: Development of the Water Quality Control Policy for Implementation of the Bay Protection and Toxic Cleanup Program. State Water Resources Control Board, Division of Water Quality, Sacramento, CA.

Wright, T. (1992) "Evaluation of Dredged Material for Open-Water Disposal: Numerical Criteria or Effects-Based?" IN: Handbook of Dredging Engineering, Herbich, J. (ed), McGraw-Hill, NY, pp 9-59 - 9-67.